D. Oxidative Stabilization of PAN Fiber Precursor

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Objectives

- Develop an improved technique for oxidizing carbon fiber precursor with increased line speed, reduced carbon fiber cost, and reduced equipment footprint.
- Verify that produced fiber properties satisfy automotive and heavy-vehicle manufacturers’ requirements.
- Conduct a preliminary evaluation of the new oxidation technique’s cost impact.

Approach

- Develop plasma process for oxidation in an atmospheric-pressure plasma reactor.
- Develop fiber handling protocols for continuous processing.
- Conduct parametric studies to correlate processing parameters and fiber properties.
- Characterize fibers to confirm that they satisfy program requirements.

Accomplishments

- Demonstrated the ability, in atmospheric-pressure plasma, to oxidize fiber in stages equivalent to conventional oxidation furnaces.
- Identified key process parameters, critical operating range, and modified the reactor to achieve stable operation in the required parametric space.

- Identified preferred range of feed gas compositions.
- Improved dielectric properties monitoring technology and presented a conference paper on that topic.

Future Direction

- Continue refining the reactor design and processing protocols to achieve rapid, single-stage fiber oxidation.
- Develop “prestabilization” technique.
- Develop continuous processing protocols.
- Conduct parametric studies and fiber characterization to better understand process effects and the processing window and to quantify fiber properties.
- Conduct rate-effect studies and update cost analysis.

Introduction

The purpose of this project is to investigate and develop a plasma processing technique to rapidly and inexpensively oxidize a polyacrylonitrile (PAN) precursor. Oxidative stabilization is a slow thermal process that typically consumes 70% or more of the processing time in a conventional carbon fiber conversion line. A rapid oxidation process could dramatically increase the conversion line throughput and appreciably lower the fiber cost. A related project (5.C) has already demonstrated the potential for greatly increasing line speed in the carbonization and graphitization stages, but the oxidation time must be greatly reduced to fully exploit faster carbonization and graphitization. This project intends to develop a plasma oxidation module that integrates with other advanced fiber processing modules to produce inexpensive carbon fiber with properties suitable for use by the automotive industry. Critical technical criteria include (1) 25-Msi tensile modulus, 250-ksi ultimate strength, and 1.0% ultimate strain in the finished fiber; (2) acceptably uniform properties over the length of the fiber tow; (3) repeatable and controllable processing; and (4) significant unit cost reduction in comparison to conventional processing.

Project Deliverable

At the end of this project, we will have demonstrated satisfactory fiber oxidation in a multiple-tow plasma oxidation module operating at line speed exceeding that typical of conventional carbon fiber conversion lines.

Technical Approach

We are investigating PAN precursor fiber oxidation by “direct exposure” in a nonequilibrium, nonthermal plasma at atmospheric pressure, with the fiber transported through the plasma. Plasma processing is thought to enhance oxygen diffusion and chemistry in the PAN oxidation process. Atmospheric pressure plasma provides better control over the thermal environment and reaction rates than does evacuated plasma, in addition to eliminating the sealing problems accompanying evacuated plasma processing. Various fiber characterization tools and instruments are used to conduct parametric studies and physical, mechanical, and morphological evaluations of the fibers to optimize the process. An evacuated plasma reactor is useful for bench-scale studies because it allows a greater degree of manipulation and control over reactive species and related parameters. Early in the project, processing tests were conducted in an evacuated plasma reactor, and that same reactor is now used for conducting the bench-scale parametric studies.

Atmospheric-Pressure Plasma Processing Results

Exposure in plasma at or near atmospheric pressure provides superior thermal control because the gas flow should convectively heat or cool the fibers. This is deemed particularly important to avoid fiber melting from the exothermic reactions associated with the PAN cross-linking that occurs during stabilization. However, the mean free path of the chemically reactive species is shorter by orders of magnitude than it is in an evacuated environment, and this makes it very difficult to find a combination of process parameters that will oxidize the fibers with acceptable residence time.

Conventional PAN oxidation is typically accomplished in three or four thermal stages (stages can be physically separate furnaces or zones in a single physical furnace) in air, at temperatures increasing from about 200°C to 250°C. In FY 2004, the researchers demonstrated the ability to reproduce the oxidation advancement in each of conventional furnaces two, three, and four. The virgin PAN is chemically fragile; hence, we have not yet discovered a satisfactory nonthermal processing protocol that reproduces the oxidation advancement in the first conventional furnace. Subsequent experiments have demonstrated the ability to advance the oxidation from the beginning of furnace two through the exit of furnace three in a single, uninterrupted process. These processing results are schematically illustrated in Figure 1.

A potentially very important discovery was that the cores of plasma-oxidized fibers are more chemically stable than are those of conventionally processed fibers. Figure 2 illustrates the advancement of oxidation and stabilization through a filament cross-section. Most of the fiber must be oxidized, as represented by the outer region, before it can withstand carbonization. In thermal oxidation, the outer stabilized and oxidized region grows inward slowly, purely by diffusion. However in plasma oxidation, we have observed that oxidation over the filament cross-section is much more uniform, and the entire fiber becomes highly oxidized at a lower fiber density (fiber density is normally used as an indicator of degree of oxidation advancement). This suggests that plasma oxidation may allow onset of

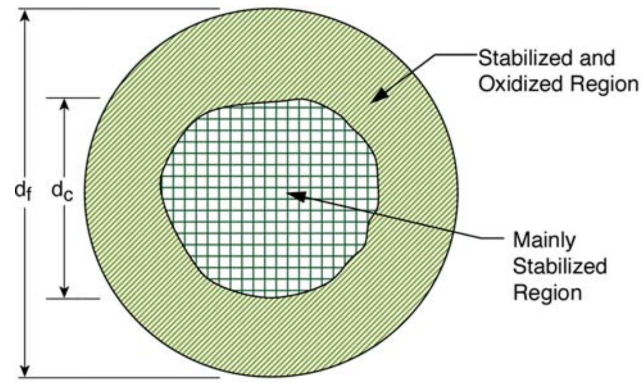

Figure 2. Illustration of advancing oxidation and stabilization through filament cross-section.

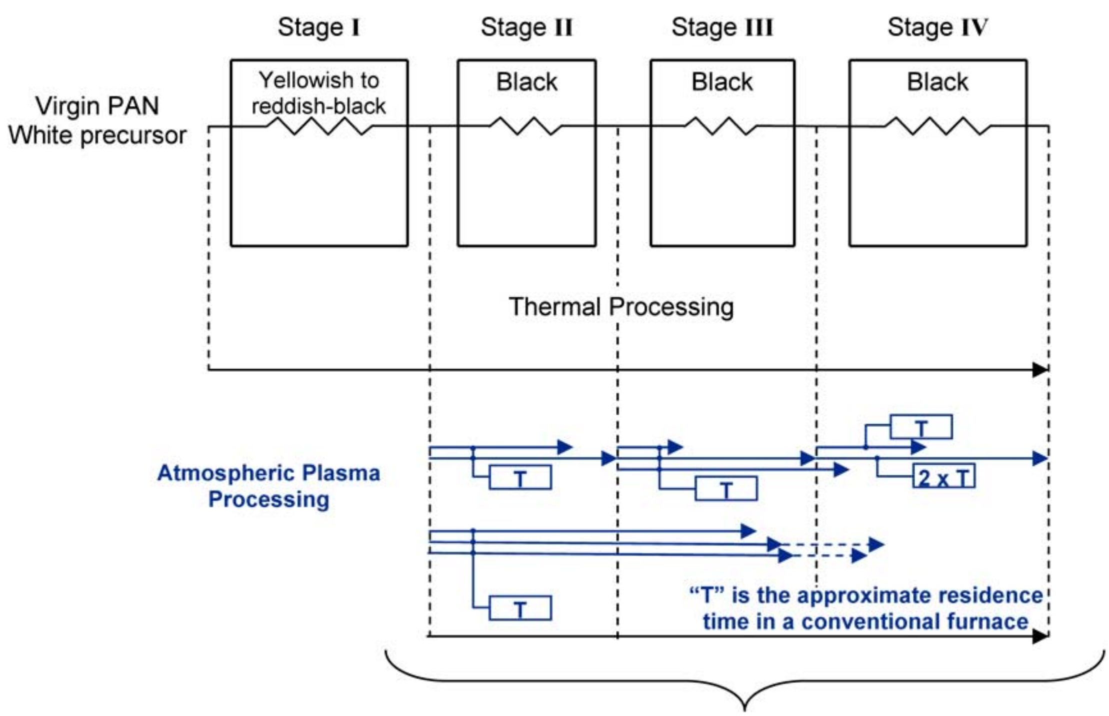

Figure 1. Schematic of conventional thermal oxidation process and progress in plasma oxidation process.

carbonization at a lower fiber density, a thesis that will be experimentally tested in future work. If carbonization can indeed commence at a lower fiber density, this could significantly reduce the residence time required for oxidation.

The researchers have made good progress toward identifying the parameters that most affect the oxidation rate and optimizing those parameters within the reactor. For patent protection and export control reasons, the detailed results are not published but are periodically disclosed to the relevant program managers in oral briefings.

Feed Gas Composition

The researchers investigated the effects of plasma oxidation with various gas compositions. It was confirmed that the chemistry can be quite sensitive to feed gas composition, as illustrated in Figure 3. A wide range of feed gas compositions were investigated and the results recorded. Specific compositions and processing parameters are not published for patent protection and export control reasons.

Instrumentation

During this reporting period, the researchers continued developing techniques and hardware for measuring the fiber dielectric properties over a selected range of oxidation processing conditions. A dielectric measurement system, shown schematically in Figure 4, was validated. Several temperature control problems were identified and corrected by adjusting control and operational parameters, modifying hardware, and changing the PAN cross-section in the instrument chamber. A large number of runs were conducted with PAN partially oxidized to differing degrees. The real and imaginary parts of the dielectric constant correlated well with the degree of PAN oxidation. A paper on this topic was presented at the 2004 SAMPE Symposium and Exposition in Long Beach, California.

The researchers began creating a dielectric properties database for 3k and 80k PAN fiber tows that were partially oxidized in varying degrees by conventional means. Plasma-oxidized fiber properties can later be compared against this database as a selector for fiber specimens that will be further characterized by more time-consuming spectroscopy techniques.

The researchers need a rapid turnaround technique for indicating oxidation trends, to quickly assess whether various parametric processing trials have successfully advanced the oxidation. Density measurements are frequently used by fiber manufacturers. In this project, dielectric measurement

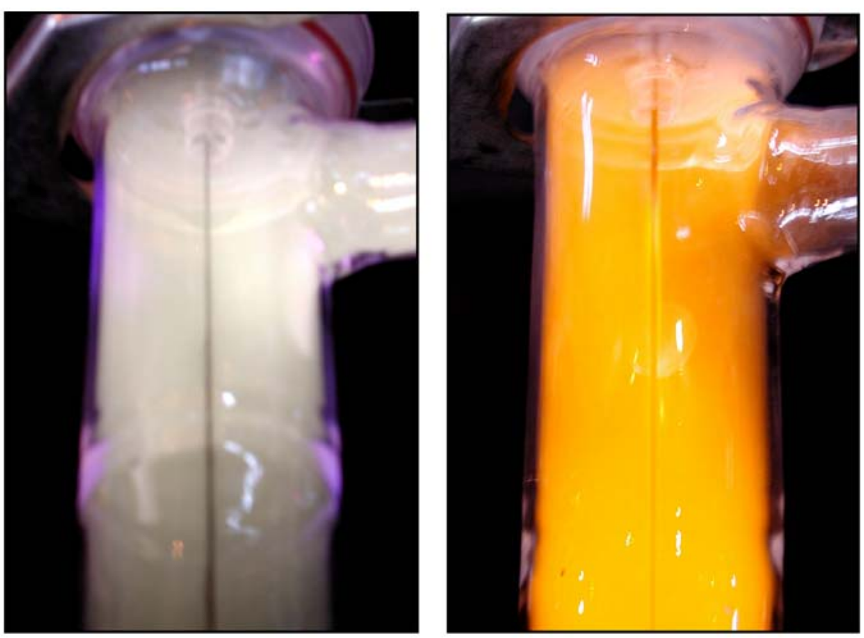

Figure 3. Plasma with two different feed gas compositions in evacuated plasma reactor.

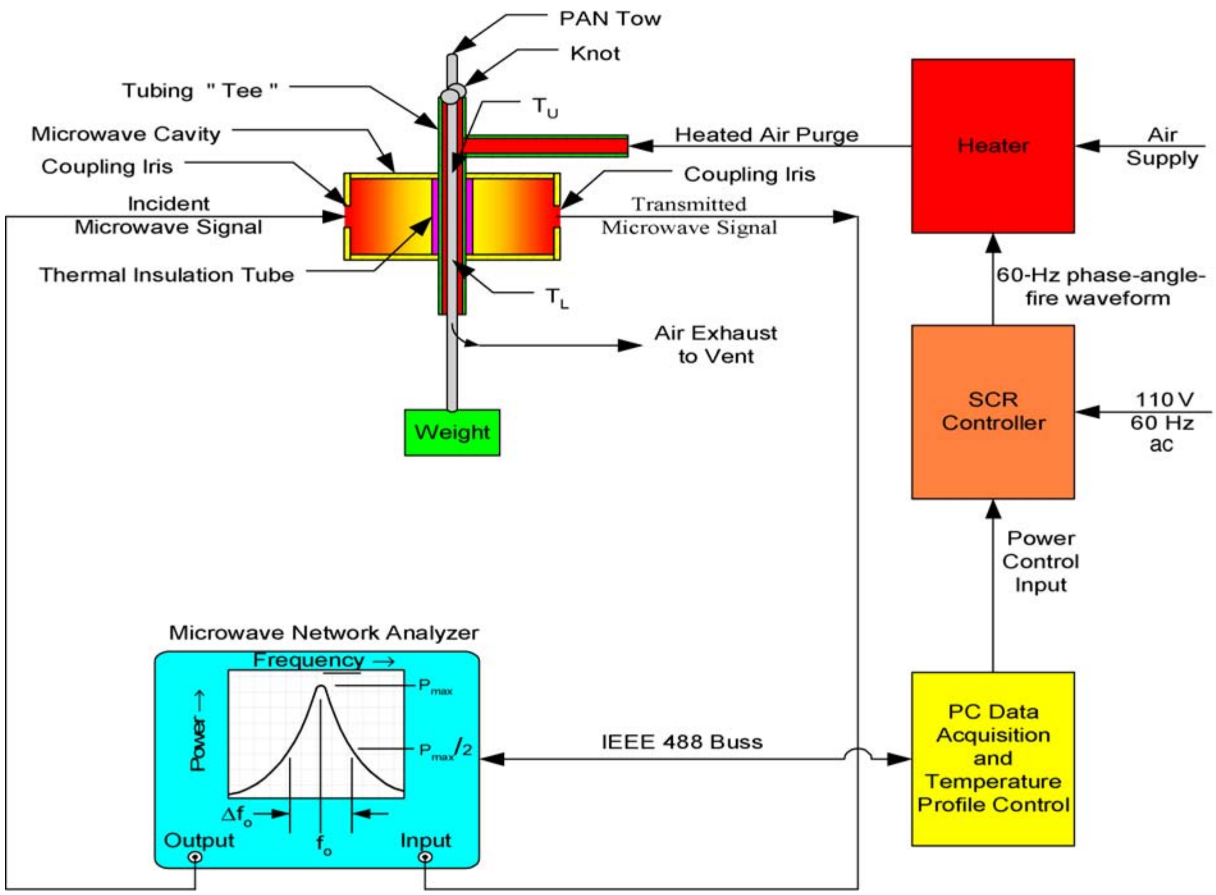

Figure 4. Dielectric measurement system schematic.

equipment and techniques have been successfully developed and validated, and morphology measurements are also used to characterize the fibers. However density, dielectric, and morphology measurements all have turnaround times of hours to days because of measurement duration, instrument cost and location, required operator skill, and/or instrument time-sharing. The fiber changes color, starting from white and successively darkening until it turns completely black after it is about 10–20% oxidized. Therefore, color is a reasonable progress indicator in early oxidation, but another technique is needed for the remainder of oxidation. The researchers investigated direct current (dc) electrical resistance measurement as an oxidation progress indicator. The very high tow resistance (10^{12}–10^{15} Ω) is beyond the capability of most resistance meters and can be accurately measured only under exceedingly well-controlled environmental conditions. A high resistance meter was purchased and tested. The PAN fiber must present the most conductive path between measurement terminals to achieve accurate resistance measurement. Because moisture, and even air, can provide a conductive "short," the researchers concluded that dc resistance measurements are too unreliable, even with ultra-high-resistance rated meters. The researchers are still searching for a good, inexpensive, and rapid turnaround technique for monitoring the relative oxidation progress.

Economics

During FY 2004, Kline and Company completed a cost study of DOE's entire carbon fiber development program, estimating profitable selling prices for baseline technology and if various technologies under development were implemented (see 4.B). Kline's estimates generally indicated that advanced oxidation techniques should reduce the fiber selling price by about 6%–8%. These estimates, however, were based on a line speed comparable to that of conventional conversion lines. Rough calculations suggest that if we can achieve much higher line speeds, the savings could increase dramatically. We have not discovered any inherent physics limits that would prevent us from achieving a large increase in conversion line speed using plasma oxidation and microwave-assisted plasma carbonization.

Education

The materials characterization has been conducted in partnership with the University of Tennessee's (UT's) materials science department. Two UT graduate students were engaged to provide characterization support to the project.

Partners

Oak Ridge National Laboratory (ORNL) gratefully acknowledges contributions to this project by Fortafil and Hexcel. Both have generously provided raw materials and offered technical consultation. An updated materials transfer agreement was executed with Hexcel during this reporting period. Additionally, technical and programmatic consultation has been provided by U.S. Council for Automotive Research's (USCAR's) Automotive Composites Consortium and by Delphi Corporation.

Conclusions

The development of plasma-based oxidation technology has achieved a major milestone by demonstrating feasibility of plasma processing to oxidize PAN precursor fibers. Preliminary data suggest that the plasma oxidation process may allow earlier onset of carbonization, thus reducing oxidation residence time. Understanding of the parametric processibility space has grown substantially during this period. Preliminary economics studies support the value of research in advanced oxidation. The researchers expect to demonstrate continuous plasma processing, and continue growing our understanding of the plasma oxidation process and its benefits in FY 2005.